Large Scale Fixed Bed Ion-Exchange System for Removing Strontium-90 from Fluid Milk. II. Compositional Studies[1]

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Abstract

Nine runs of 45,400 liters of milk per 8-hr day have been made, resulting in an average of 91.7% removal of environmental levels of Sr^{90}. No significant increase in microbial population occurred during the runs, and the keeping quality of the processed milk appeared to be satisfactory. Flavor scores averaged 37.2 after processing, a decrease of 0.6 from the untreated samples. Minor compositional changes were found in freezing point, curd tension, titratable acidity, and ash. There was an increase of 0.36% in concentration of potassium citrate, due to acidification and neutralization of the milk. The remaining components tested showed insignificant changes.

This report describes work which is a continuation of studies made at the Public Health Service Robert A. Taft Sanitary Engineering Center at Cincinnati (15, 16) and the Beltsville Laboratory of the USDA (4–6). Bench and pilot scale results indicated that the fixed bed ion-exchange system could substantially reduce the level of Sr^{90} in milk. Investigations were, therefore, made to determine the commercial feasibility and practicality of the Beltsville pilot plant process for removing radionuclides from milk. These results have been described in the preceding report (19), whereas this one will be confined to the analytical results.

Experimental Procedures

For each run, the milk was shipped in tankers, each holding about 15,876 liters. Samples were taken from each tanker, from pipe lines as the milk was pumped to the columns, from pipe lines after leaving the columns, and from the pasteurized processed milk in the tankers as they left the plant. The processed milk was spray-dried and sold for animal feed.

Radiological assays were made by Controls for Radiation, Inc., Cambridge, Massachusetts, following the procedure of Martell (12) for the rapid assay and that of Harley (9) for the longer assay.

Protein was determined by a semimicro-Kjeldahl method (13) and lactose by means of a polarimeter (8). Citric acid (11), phosphorus (7), and iron (3) were determined colorimetrically. Sodium and potassium were determined by flame photometry (10). Total concentrations of calcium and magnesium were determined by direct titration with EDTA (17). Calcium was then determined by permanganate titration of calcium oxalate (3) and magnesium estimated by difference. Chlorides (18) and titratable acidity (2) were determined by titration. Freezing points were obtained with the Fiske Cryoscope (3). Curd tensions were made using the Cherry-Burrell Curd Tension Meter following ADSA procedures (1). Fat and total solids tests were made by the Mojonnier Tester (14). Ash was determined at 550 C (3). A Beckman Model G and a Beckman Zeromatic were used for estimating pH.

Bacteriological procedures were followed as described in Standard Methods (2). Standard plate counts were made at 32 C. Violet red bile agar enumerated coliform bacteria and Medium 110, staphylococci.

All determinations were made in duplicate or quadruplicate. Results will be discussed and evaluated on the basis of radiological, chemical, microbiological, and organoleptic changes.

Results and Discussion

Strontium-90 removal. Efficiencies of Sr^{90} removal from milk for seven 45,400-liter runs and one 90,000-liter run are presented in Table 1. Removal efficiency varied from 86.0 to 96.9% and averaged 91.7% for a total of 413,000 liters of milk processed. Generally, lower removal efficiencies occurred at lower environmental levels of Sr^{90}. Removal efficiencies apeared to vary seasonally.

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TABLE 1
Removal efficiency of Sr^{90} (long method) for total of 413,000 liters of milk

			Strontium-90 pc/liter			
Run no.	Date of run	Product	Raw	Average of line samples	Processed	% Removal
143	5/22/64	Skim	42.2	2.9	12.4[a]	93
176	6/24/64	Whole	36.0	1.1	1.1	97
233	8/20/64	Skim	32.9	1.6	1.8	95
246	9/2/64	Skim	43.7	2.0	2.4	95
260	9/16/64	Whole	31.0	2.3	2.1	93
288	10/14/64	Whole	25.6	2.8	2.6	90
052	2/21/65	Whole	31.8	5.2	4.5	86
056A	2/25/65	Whole	30.9	2.8	2.8	91
056B	2/25/65	Whole	34.4	5.0	4.6	87
Average long method results			34.3	2.8	2.7	91.7
Average short method results			33.1	3.5	3.8	88.5

[a] Value excluded from calculations.

To obtain results on the operation of the columns as quickly as possible, a short method (12) for Sr^{90} was used which yielded results in 12 to 14 days, compared with about 8 wk for the Standard Method (9). These results, shown at the bottom of Table 1, indicate that the Short Method can be used with confidence as a control method, although it tends to underestimate the true level in raw milk and overestimate it in processed milk.

As a check on the reliability of the Sr^{90} assays and sampling procedures, an accountability study is reported for all runs in Table 2. The Sr^{90} in the regenerant solution was found to be $98 \pm 18\%$ of the Sr^{90} in the milk processed. The wide variation in some of the results is probably due to the problem of obtaining a representative sample of the regenerant solution as it leaves the column.

Chemical changes. In early runs, results obtained on the processed milk were corrected to allow for dilution of the processed milk with water, both that remaining in the column at the start of the run and that added with the 20% citric acid and 6% potassium hydroxide solution as described by Edmondson et al. (6). When this dilution correction was made, there was still an apparent decrease in protein, fat, lactose, and certain other constituents in the processed milk. When the increase in solids in the processed milk due to the addition of potassium and citrate ions was included in correction calculations, the amount of the original components in the processed milk could be accounted for.

Results shown in Table 3 demonstrate this point. The data are the average of six whole milk runs. Protein in the raw milk, for example, was found to be 3.29% before and 3.32% after processing and correction for dilution

TABLE 2
Accountability of Sr^{90}

Run no.	Liters milk processed	Milk pc/liter	Total pc to column ($\times 10^3$)	Liters regenerant (14 B.V.)	Regenerant pc/liter	Total pc from column ($\times 10^3$)	Per cent recovery
143	43,459	42.2	1,833	18,547	83.5	1,549	85
176	45,499	36.0	1,637	18,547	65.7	1,218	74
233	45,377	32.9	1,492	18,547	99.6	1,846	124
246	45,656	43.7	1,995	18,547	119.4	2,213	111
260	43,730	31.0	1,355	18,547	95.1	1,763	130
288	45,217	25.6	1,157	11,923[a]	94.3	1,124	97
052	45,910	31.8	1,459	11,923[b]	100.9	1,203	82
056A	43,900	30.9	1,356	11,923[c]	105.4	1,256	93
056B	44,848	34.4	1,542	11,923[d]	107.9	1,286	83
						Average	97.7

[a] Nine Bed Volumes of fresh regenerant @60 C through column to waste.
[b] Nine Bed Volumes of fresh regenerant @60 C. Last 4.5 BV of used regenerant saved for Run 056A.
[c] Four and one-half Bed Volumes of the last-used 60 C regenerant from Run 052. Then 4.5 Bed Volumes of new regenerant @60 C through column saved for [d].
[d] Four and one-half Bed Volumes of 60 C, the last-used regenerant from Run 056A and 4.5 Bed Volumes new regenerant @60 C.

TABLE 3

Comparison of raw and processed milk
(Average of 6 runs totaling 278,300 liters of milk)

Analysis	Raw	Processed[a]	Difference
Protein *(%)*	3.29	3.32	+0.03
Ash *(%)*	0.74	0.90	+0.16
Curd tension *(g)*	35.0	0.0	−35.0
Sp. gr. *(15.56 C)*	1.0285	1.0280*	−0.0005
Freezing point *(C)*	−0.529	−0.556*	−0.027
pH	6.79	6.78*	−0.01
Fat *(%)*	3.68	3.69	+0.01
Total solids *(%)*	12.48	12.84	+0.36
Lactose *(%)*	4.57	4.55	−0.02
Citrate *(ppm)*	1,852	4,209	+2,357
Sodium *(ppm)*	449	403	−46
Potassium *(ppm)*	1,669	2,902	+1,233
Magnesium *(ppm)*	144	149	+5
Calcium *(ppm)*	1,209	1,299	+90
Iron *(ppm)*	0.52	0.63	+0.11
Chloride *(ppm)*	1,297	1,360	+63
Inorganic P *(ppm)*	661	654	−7
Acidity *(%)*	0.13	0.16*	+0.03

[a] $\text{Correction factor} = \dfrac{\text{Original total solids}}{\text{Processed total solids} - \text{increase in K and citrate}}$

Example: Run 260

$$1.078 = \frac{12.89}{12.43 - 0.47}$$

* Not corrected for dilution effect.

effects due to water and the potassium citrate formed by addition of citric acid and potassium hydroxide. These dilution effects averaged about 8%. About one-half of this is due to potassium citrate and one-half to water which can be removed by incorporating a small evaporator into the processing system. Of the added water, about one-half comes from the solutions used for adjusting pH and about one-half from water remaining in the columns after washing the resin.

Changes in the concentration of some of the milk constituents as the run progresses are given in Table 4. Sodium, potassium, and citrates increase, whereas calcium and magnesium decrease with increasing BV[2] of milk processed. The steady increase in citrate ions is not readily explainable. Output of the citric acid pump, the pH of the milk after acid injection, and the concentration of citric acid solution remained constant. Some preliminary pH checks on samples of the column effluent, taken prior to the neutralization step, indicated that the pH of the first portions was ca. 5.40.

[2] Bed Volume (BV) is equal to the amount of resin in column, 1,325 liters.

TABLE 4

Relation of composition of effluent to number of Bed Volumes processed
(Average of 3 runs corrected for water dilution)

No. of BV Processed	Citrate	Na	K	Ca	Mg	Sr^{90} *(pc/liter)*
	(ppm)					
1	3,608	357	2,529	1,388	183	......
3	3,522	309	2,733	1,411	166	......
5	3,693	357	2,726	1,415	170	3.5
7	3,773	376	2,668	1,390	171	......
10	3,794	386	2,660	1,395	154	2.9
15	3,865	397	2,836	1,366	121	3.2
20	3,990	415	3,002	1,241	129	2.7
25	3,905	408	3,001	1,246	126	3.8
30	4,007	411	2,902	1,221	127	4.3
Raw comp.	1,877	458	1,728	1,248	130	36.3
Processed comp.	3,822	404	2,863	1,300	140	3.3

TABLE 5

Bacteria counts on line samples of raw milk processed for removal of Sr^{90}

Sample	Run 176	Run 233	Run 246	Run 260	Run 288
	(SPC/ml × 10³)				
Raw milk					
Load 1	71	90	38	46	250
Load 2	120	77	410	98	69
Load 3	100	120	110	71	52
Start of run					
Column influent	80	50	31	39	580
Column effluent	33	30	30	39	94
Middle of run					
Column influent	66	50	140	68	59
Column effluent	56	69	320	82	110
End of run					
Column influent	120	95	130	41	67
Column effluent	140	79	110	150	86

Average of load counts, 115,000/milliliter.
Average of influent counts, 108,000/milliliter.
Average of effluent counts, 95,200/milliliter.

As the run progressed, this value appeared to decrease to 5.25. This observation should be studied further, since it would indicate that citrate may become more complexed in the column at the start than at the end of the run.

The principal difference, as seen from Table 3, between the raw and the processed milk from a compositional standpoint, is due to addition of approximately 0.4% of potassium citrate. In the six whole milk runs, there was an average increase in citrate ion of 2,357 ± 584 parts per million, or approximately 0.24%, and 1,233 ± 233 parts per million of potassium, or approximately 0.12%, resulting in a total increase of 0.36 ± .08%. This figure checks well with the increase of 0.36 ± .08% in total solids.

Reduction in curd tension is attributed to the potassium citrate content.

Observed freezing point values of the processed milk were corrected for the dilution effect of an estimated 4% added water by adding a value of − 0.021 C. Specific gravity results were also corrected by adding 0.0022 to observed values, whereas 0.005% was added to the titratable acidity results. After making these empirical corrections, a study of the data revealed a significant increase in titratable acidity ($P < 0.1$), in specific gravity ($P < 0.05$), and a significant decrease in freezing point ($P < 0.01$).

Bacterial counts. Bacterial counts on line samples of raw milk taken before and during processing for five runs are summarized in Table 5. These results do not show any increase in count which can be attributed to the operation of the columns. The average of the load counts was 115,000; average of the line samples taken from milk being pumped to the columns was 108,000; and the average of line samples taken from the columns was 95,200. While the differences among these averages are not statistically significant ($P > 0.5$), these results suggest that some microorganisms may be removed from the milk during passage through the columns at pH 5.3. These results also indicate that the columns can be operated under satisfactory sanitary conditions.

Results of bacterial counts made on the pas-

TABLE 6

Bacterial counts on processed pasteurized milk after removal of Sr^{90}

Sample	Run 176	Run 233	Run 246	Run 260	Run 288
Tank 1					
SPC/ml	<3,000	<3,000	10,000	<3,000	<3,000
Coliform/ml[a]	2	0	0	117	0
Staph./ml[b]	1	2	1	3	0
Tank 2					
SPC/ml	<3,000	<3,000	3,600	<3,000	<3,000
Coliform/ml	0	0	17	6	0
Staph./ml	1	0	1	1	0
Tank 3					
SPC/ml	<3,000	<3,000	<3,000	4,500	<3,000
Coliform/ml	66	0	18	1	0
Staph./ml	2	0	0	0	0

[a] All colonies appearing on Violet Red Bile Agar.
[b] All colonies appearing on Staph. Medium 110.

TABLE 7

Variation in flavor score with Bed Volumes processed for Sr^{90} removal

Sample	One day/4.4 C[a]	Ten days/4.4 C[b]
Raw comp.	37.8	
5 BV	36.9	36.1
10 BV	37.0	36.2
15 BV	37.1	36.6
20 BV	37.3	36.2
25 BV	36.9	36.4
30 BV	37.3	35.8
Processed comp.	37.2	35.9

[a] Average of seven runs.
[b] Average of three runs.

teurized processed milk after removal of Sr^{90} are shown in Table 6. In a few cases, the milk had to be pumped from one tank to another, to obtain representative samples. Because of this unusual procedure, high coliform counts were encountered, once on Run 176 and once on Run 260. In general, however, the bacteriological results indicate satisfactory processing control and equipment sanitation after pasteurization of the processed milk.

Organoleptic changes. In the early runs, owing to problems encountered in the pumping of the milk and the control of pH to and from the columns, a greenish cast was observed in the processed milk (Runs 143 and 176). Also on these two runs, flavor was impaired. Run 143 had a flavor score of 30 after processing, and Run 176, 35.8. After operating conditions were stabilized, flavor scores were substantially improved, and the greenish cast of the processed milk could be recognized only by direct comparison with the untreated control samples.

Results of flavor scores taken from line samples after processing and the processed composite samples for seven runs are presented in Table 7. The milk was submitted to a trained panel of from five to seven members. The flavor score-card used was that of the American Dairy Science Association. Table 7 shows that the average score of the milk before processing was 37.8, and 37.2 after processing. The average decrease in flavor score due to processing was found to be 0.6 point, not considered large enough to indicate a flavor problem. Samples of processed pasteurized milk from three runs were held in the refrigerator for ten days and again submitted to the flavor panel for flavor evaluation. Although a slight decrease in score occurred, the keeping quality properties of the processed milk are considered to be satisfactory.

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